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CHEMICAL CONVERSION OF WOOD AND CELL-
ULOSIC WASTES

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CHEMICAL CONVERSION OF WOOD AND CELLULOSIC WASTES

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment—air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

studies on the effects of environmental contaminants on man and the biosphere, and

- a search for ways to prevent contamination and to recycle valuable resources.

As part of the effort to reduce the problems created by municipal solid waste, the project reported here was undertaken to investigate practical methods to convert, through thermal reaction, cellulosic waste to useful products such as levoglucosan, levulinic acid, glyoxal, and active carbon.

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ABSTRACT

The purpose of this project was to investigate practical methods for conversion of cellulosic wastes to useful products such as levoglucosan, levulinic acid, glyoxal and active carbon through thermal reactions. The cellulosic wastes investigated were recovered from municipal refuse by air and water classification. The recovered materials were analyzed and characterized in terms of their cellulose, lignin, extractives and ash contents. These data indicated the extent of contamination and the limits for potential conversion of the recovered materials to chemical products.

Thermal degradation reactions were carried out with pure cellulose as ideal samples and several types of recovered materials. These reactions gave a variety of products that could be separated into char, tar, volatile liquid and gas fractions.

It was shown that useful grades of active carbon could be obtained from the chars. The tar from pure cellulose contained significant amounts of levoglucosan and related materials, however, the contaminants in the recovered materials drastically reduced the yield of the sugar compounds in the tar. The volatile liquids obtained under normal pyrolytic conditions consisted of a variety of compounds in small or insignificant, individual yields, therefore, acid and alkali catalysts were used to direct the degradation reactions. Acid catalysis, under aqueous conditions, provided reasonable yields of levulinic acid, and alkali catalysts under pyrolytic conditions gave intractable materials. Further investigation of the volatile liquid and gas fractions was prevented by economic constraints of the project. Although it should be noted that gasification of enormous quantities of cellulosic and organic waste from forestry, agriculture and other sources under the present condition of fuel shortage merits serious consideration.

This report was submitted in fulfillment of Project Number EPA 300652 (formerly 00370-02) by the University of Montana Wood Chemistry Laboratory under the (partial) sponsorship of the Environmental Protection Agency. Work was completed as of September 1973.

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I. CONCLUSIONS

The utility of cellulosic waste recovered from municipal refuse is greatly limited by the physical damage and chemical contamination of the fibers. Under these circumstances, priority should be given to development of better recovery methods and, whenever possible, initial segregation of waste paper from other refuse.

The possibilities for chemical conversion of recovered cellulosic materials include production of absorbent carbon, production of levulinic acid and gasification. Each of these possibilities strongly depends on the economic and social circumstances.

Production of the absorbent carbon can be envisaged as a part of an integrated municipal system which includes the treatment of air and water.

Levulinic acid depends strongly on the development of market and related chemical technology.

The gasification process, which was not investigated, may be justified by a drastic shortage of natural gas and a large supply of forestry residues and other vegetable wastes.

II. RECOMMENDATIONS

This report provides scientific data on the technical feasibility for chemical conversion of cellulosic wastes to several products. The authors recognize that implementation of these processes not only requires technical possibility but also, economic and social desirability. Therefore, recommendations or action on the basis of the technical feasibility alone would not be justified.

However, it is strongly recommended that this information and the related data on thermal reactions, some of which is referred to in this report, should be seriously considered in any action spurred by the social needs and economic circumstances.

III. INTRODUCTION

Municipal solid waste commonly contains materials from residential, commercial and institutional sources and amounts to about 360 million tons per year in the United States, or roughly 10 percent of the 3.5 billion tons of solid waste generated annually from all sources.¹ About half of the municipal waste is composed of cellulosic materials, particularly the paper products. The problems of adequate disposal of these wastes are compounded by the rapid development of our technology and economy, which results in increasing production, consumption and discarding of paper products. The tremendous increase in production of paper and paper products (see Table 1) and escalation of the paper industry from rags to riches was due to scientific and technological developments showing that paper could be manufactured from abundantly available wood rather than from the tight supply of rag.² Now it seems that this development has been carried out to the extreme and the time has come to rediscover or find new methods for using waste cellulosic materials.

Currently, economic considerations dictate that disposal techniques be as inexpensive as possible and they differ little from those of past centuries, landfill and incineration. In direct costs, an estimated \$6.4 billion was spent last year by municipalities for collection and disposal of wastes.¹ But 90 cents of each dollar is relegated to the labor and transportation cost of collection and only 10 cents is left for the actual disposal.³ The indirect costs of these practices in terms of pollution sources, health hazards, lost resources and degraded land have been overlooked in past years but must be considered in the light of increasing environmental awareness.

Table 1. WORLD PRODUCTION OF PAPER AND PAPERBOARD
(from reference 2)
(million tons)

Year	America	Europe	Others	Total
1913	6	6	1	13
1935-1938 (average)	16	12	3	31
1946	24	8	2	34
1947	26	9	2	37
1948	27	10	3	40
1949	26	11	4	41
1950	30	13	4	47
1951	32	14	5	51
1952	30	13	6	49
1953	32	15	6	53
1954	33	17	6	56
1955	36	18	9	63
1956	38	19	9	66
1957	37	20	11	68
1958	37	21	11	60
1959	40	22	14	76
1960	41	25	15	81
1961	43	26	17	86
1962	45	27	17	89
1963	48	29	19	96
1964	51	31	21	103
1965	54	32	23	109
1966	56	34	26	116
1967	56	35	26	117
1968	59	37	28	124

Recently, over 95 percent of the landfill operation and over 75 percent of the incinerators in the United States were found to be unacceptable in terms of the air and water pollution problems that occur with their operation.⁴ Landfills commonly leached contaminants into nearby streams or ground water while incinerators usually lacked adequate air pollution control equipment. Incineration also does not necessarily destroy pathogens associated with solid wastes, as is generally assumed. A recent study showed significant numbers of these organisms survive in incinerator residues from several incinerators.⁵ Diseases borne by rodents, flies and mosquitoes, commonly found at landfill operations, include typhoid, amebic dysentery, salmonellosis, trichinosis, and encephalitis.⁶ The amount of resources lost that could be reclaimed and the amount of property degraded by our present disposal techniques can be offset somewhat by reclaiming the landfill area and developing it or by recycling some of the discarded materials. Unfortunately, the vast percentage of municipal solid waste is not reused nor are the landfill areas reclaimed as community assets.

Realizing the obvious shortcomings of incineration and landfill operations, technology is being developed to economically sort or classify solid wastes into some of its various components, recover and reuse some of the fractions and discard the remainder. The greatest difficulty lies in the complexity of solid wastes. As shown in Table 2,⁷ small percentages of a variety of materials are present and they hamper the efficient recovery of the easily recyclable components, paper, glass and metals.

Table 2. TYPICAL MUNICIPAL SOLID WASTE COMPOSITION

Paper products	48%
Glass and ceramics	8
Metals	9
Food waste	19
Garden waste	4
Plastic, rubber, leather	4
Textiles	3
Wood	2
Ash, rocks, dirt	3
	<u>100%</u>

Two of the more promising recovery methods are the Zig-Zag Air Classifier and the Hydropulper System, which will be discussed later. Unfortunately, both of these processes are limited in their abilities to recover waste paper suitable for recycling as new paper. The reclaimed fibers are either too contaminated or lack sufficient strength to be incorporated into pulp. These problems have plagued paper recovery operations and most of the recycled paper in the United States is derived from paper wastes segregated from other wastes at the source of their generation.⁸ In countries with cheaper labor markets, where manual sorting is feasible, the recycling rate is much higher than for the U.S., as shown in Table 3.⁹ In fact, it has been estimated that as much as 66 percent of the paper products discarded is potentially reclaimable.¹⁰

Table 3. RECYCLED WASTEPAPER IN THE UNITED STATES
AND OTHER COUNTRIES, 1971

Country	Percentage of Production
West Germany	46%
Japan	37
United Kingdom	37
France	33
United States	20
Canada	4

However, paper production is only one of several possible recycling routes which can be divided into two broad categories, physical utilization and chemical conversion.

Utilization techniques depending on physical characteristics take advantage of the strength and flexibility of paper fibers, as well as their refinability and brightness index. Any contamination or degradation of the fibers results in their being used in a lower grade product. Eventually, the lowest grade papers are reused as filling material for paperboard, roofing tiles, insulation and similar products. For these uses, strength of the fibers is not important but they can not contain too many contaminants. Since most paper waste consists of lower grade papers, the rather limited market for recovered fibers of this type has spurred research to develop new products from them such as building blocks, hardboard, fire logs, asphalt and sewer pipes.¹¹

Chemical conversion of waste fibers displays a wider variety of applications than physical utilization. Primarily, the chemistry is directed at the reactions of cellulose, the β -D-glucose polymer that is the largest constituent of wood and, in turn, paper. But the many types of reactions of the cellulosic materials allows several methods to be explored. A few of the newer techniques under study involve hydrogenation to fuel oil¹² and gassification by pyrolysis followed by combustion of the gases in either a turbocharger or a waste heat recovery furnace¹³ as means of recovering stored energy. Others include microbial digestion to produce either a single-cell protein fodder¹⁴ or compost.¹⁵ Hydrolysis to glucose and destructive distillation are two of the chemical processes attempted in the past but most of these attempts have failed over and over again, because of known deficiencies and problems.¹⁶ Hydrolysis of sawdust to sugar, for instance, originally was developed in Europe under the stimulation of war economy and after more than 50 years of developmental efforts by various countries, it is now amply clear that this process is too expensive and cumbersome to survive under the conditions of free economy.

The newer methods of conversion are still under study but to compete against the present alternatives of waste disposal, a chemical conversion process should meet several criteria:

- A. It must be cheap and not require extensive facilities.
- B. It must produce a useful product to defray production costs.
- C. It must not create unsolvable pollution problems.
- D. It must work with substantially impure raw materials.
- E. It must be rapid in order to process large quantities in a reasonable time.

The previously mentioned conversion methods, for the most part, fail to meet these considerations. The chemical approaches remaining become severely limited and only few suggest themselves as being adaptable enough to deserve further study.

Pyrolysis and hydrolysis are the most outstanding possibilities and offer varying advantages. From a processing point of view, the pyrolytic methods are inherently more practical and efficient for bulky and low priced materials than solvent or aqueous reactions. However, from the production point of view, they are generally unspecific and uneconomical for isolation of individual compounds (other than charcoal). Hydrolytic methods yield specific products but processing costs are usually high. Within the extremes of each process, though, there are possibilities for production of useful chemicals in an economically feasible manner.

IV. PYROLYSIS

Pyrolysis of cellulose provides a mixture of volatile materials, tarry products and char. The proportion of each fraction and its composition is highly dependent on the conditions of the reaction and the extraneous materials which could be added or accompany the cellulosic substrate. Since different pyrolysis products are formed through competing chemical pathways, catalytic blocking of the undesirable side reactions or promotion of the desirable one should increase the specificity of the thermal reactions and the yield of the individual products. This amounts to the same approach as the catalytic cracking of the petroleum residuals by the oil industry.

to achieve this goal, it is necessary to determine what are the competitive reactions involved in the pyrolysis of the cellulosic materials, how they relate to the composition of the substrate and whether they could be catalytically blocked or promoted. In view of the complexity of the problem, previous isolated attempts and short cuts were not successful and systematic studies were sidetracked as being too tedious. However, with the recent development of powerful instruments for chemical and thermal analysis and progress in related physical sciences, the time has come that a systematic approach towards solving this problem could be adopted.

Considerable progress has been made on this program in this laboratory. The results obtained are discussed with sufficient experimental data in a number of publications¹⁷⁻³⁵ and presented at several national and international meetings. These data which are summarized here provide a basis for the investigations under the EPA project.

Initially, cottonwood, a common hardwood species in Montana, was selected as a representative of complex woody tissues and was chemically analyzed to its components, cellulose, xylan, lignin extractives and ash. Thermal analysis of this material showed that pyrolytic behavior of the complex cellulosic substance represents the behavior of its components. Furthermore, it was shown that pyrolysis of cellulose begins at about 300°C and proceeds very rapidly at 350°C. Xylan, which is the principal hemicellulose of hardwoods, starts decomposing at about 200°C but decomposition is completed over a wider temperature range than that of cellulose. Lignin is also pyrolyzed over a wider temperature range, but the pyrolysis leaves a large residue. Thus, the volatile products originate mainly

from the hemicellulose and cellulose fractions, and the char is derived mainly from lignin. The ash content affects pyrolysis of the cell wall polysaccharides and increases the amount of char at the expense of the volatile combustible products.¹⁸ Further work on this subject, especially the effect of the ash content on the pyrolysis of the plant materials, has been conducted at the Northern Forest Fire Laboratory of the Forest Service in Missoula. These studies have shown a significant and direct relationship between ash content and pyrolysis of a natural fuel.

To investigate the thermal behavior of xylan and cellulose, a variety of model compounds including α -D-xylopyranose, substituted phenyl β -D-xylopyranosides, 1,6-anhydro- β -D-glucopyranose (levoglucosan), several phenyl β -D-glucopyranosides and the corresponding 2-deoxy-D-glucosides were studied. Initial chromatographic studies showed that the pyrolysis products of xylan and cellulose are essentially the same as those of D-xylose and D-glucose derivatives respectively, except for some minor quantitative variations. These experiments showed the relevance of the selected model compounds. They also confirmed the conclusion derived from the following data that the polysaccharides are first broken down to the same sugar moieties that are present in the selected model compounds.

The sequence of events which take place when carbohydrate molecules are heated is revealed by thermograms of the various model compounds exemplified by that of phenyl glucoside, shown in Figure 1. These thermograms show that heating first results in endothermic physical changes of the substrates such as drying¹⁹ and transition to new forms with higher energy, heat capacity and entropy, while the extent of hydrogen bonding is lowered.²⁰⁻²³ At higher temperatures, the physical changes

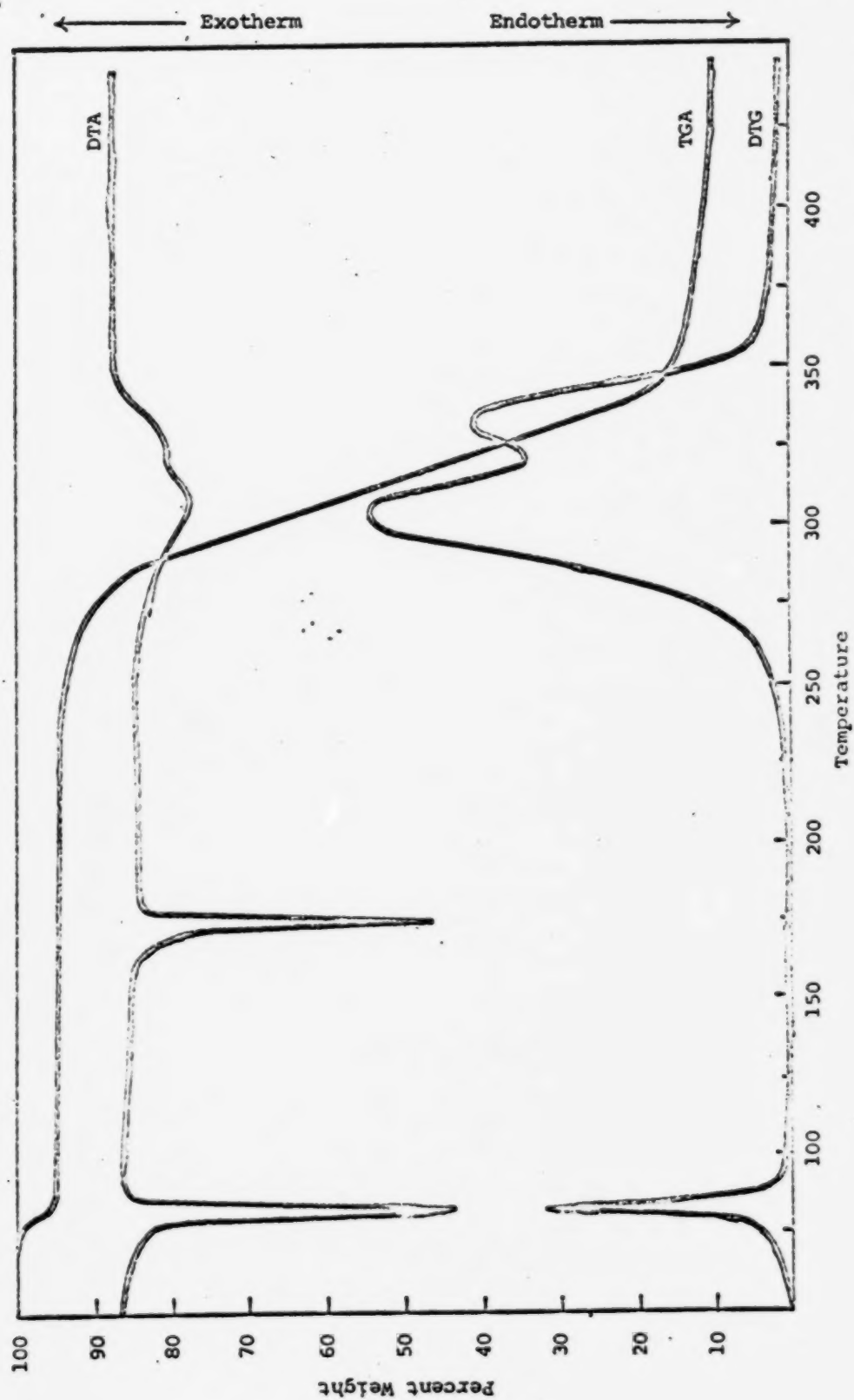


Figure 1. Thermogram of phenyl β-D-glucopyranoside (from reference 19)

are followed by cleavage of the existing glycosidic bond^{19,24} through nucleophilic displacement by free hydroxyl groups. The transglycosylation reaction gives anhydro sugars and low molecular weight randomly linked oligosaccharides.²⁵⁻²⁸ The transglycosylation products are further decomposed and evaporated as a variety of pyrolytic products, leaving a charred residue. Figure 2 shows the sequence of these events for phenyl β -D-glucopyranoside. This phenomenon accounts for the formation of essentially the same pyrolytic products from the polysaccharides and from corresponding model compounds with the same sugar unit. It also explains why gentle pyrolysis of cellulose under vacuum provides a high yield of levoglucosan. Apparently under these conditions, the glycosyl radicals which are generated react internally to give the anhydro sugar; whereas, when the glycosyl units are not removed from the reaction mixture by vacuum, they react with each other to form condensation products that are decomposed on further heating.

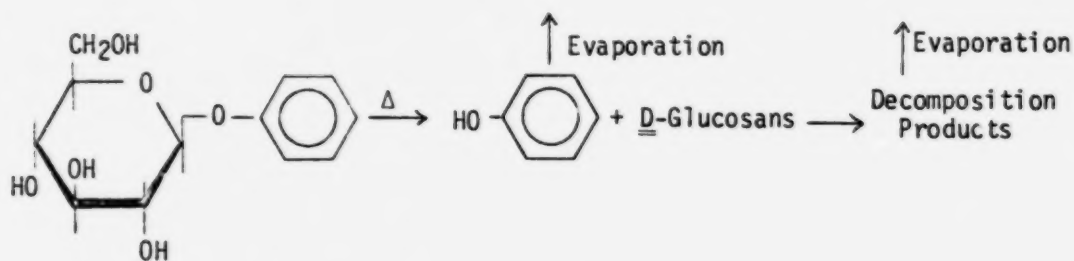


Figure 2. Pyrolytic reactions of phenyl β -D-glucopyranoside

Some of the factors which influence the cleavage of the glycosidic bonds and the mechanism and kinetics of this reaction were investigated by synthesizing a number of phenyl glycosides having different substituents on the glycosidic group or some variations in the sugar moiety. The

decomposition characteristics of these compounds were determined by dynamic thermal analysis methods, and their overall rates of pyrolysis were studied with isothermal thermogravimetry and ESR spectroscopy which reflected the loss of volatile degradation products and forming charred residues containing free radicals, respectively. These investigations showed that the temperature and the rate of decomposition of glycosides are directly related to the electron density of the glycosidic bond. In other words, the glycosides containing a better leaving group are decomposed at a lower temperature (in dynamic analysis) or at a faster rate (in isothermal analysis). Furthermore, the isothermal studies revealed almost identical overall energies of activation (~ 42 Kcal/mole) for evaporation of volatile decomposition products and for the formation of free radicals in the residue. These data^{19,24} show that the pyrolysis process (in absence of additives) is controlled by a rate-determining step which involves the glycosidic group. In other words, under the uncatalyzed pyrolytic condition, cleavage of the glycosidic group is closely followed by other thermal reactions, including decomposition to volatile products and char formation, which show the same overall energy of activation. The close association of the pyrolytic reactions could be also seen in the thermograms of the glycosides, which generally contain a single decomposition peak.

A series of pyrolysis experiments were carried out using zinc chloride as a Lewis acid catalyst.^{23-25,29} These experiments showed that the acidic catalyst substantially reduces the temperature at which the cleavage and polymerization of the glycosidic group takes place. Consequently, the subsequent decomposition reactions proceed through a low energy pathway,

involving dehydration and charring rather than the higher energy pathway involving fragmentation to combustible volatile products. Dependence of the pyrolytic pathways on the temperature of decomposition was further demonstrated by comparing the thermograms of a free sugar (α -D-xylopyranose) with its glycoside (phenyl β -D-xylopyranoside). This comparison showed that the decomposition of the former compound proceeds at relatively lower temperatures and gives a substantial amount of carbonaceous residue. On the other hand, the latter compound is stable at the lower temperatures; but, when the glycosidic group is cleaved at higher temperatures, decomposition of the released sugar moiety proceeds rapidly and yields a high proportion of volatile degradation products.²⁴

The nature and mechanism of the competing pathways were explored by several methods including quantitative analysis of the various pyrolysis products formed under acidic, alkaline and normal (neat) conditions. These data showed a substantial variation in the yield of the individual products and a profound shift in the competing pathways under different catalytic conditions.²⁴ This experiment was followed by synthesis and investigation of model compounds which were isotopically labeled at different positions (1-, 2-, and 6-C¹⁴-levoglucosan).³⁰ Pyrolysis of the isotopically labeled compounds under various conditions and tracing of the decomposition products to the original molecule gave the percentage of each product derived from different sections of the molecule. By piecing together the fragmentation patterns and the yield data obtained from the previous experiment, it was possible to show the chemical reactions involved in different pyrolytic pathways.

The resulting data clearly indicate that the acidic condition catalyzes the formation of furan compounds, water and char in close analogy with the better understood dehydration reactions of carbohydrates under aqueous acidic conditions; whereas the alkaline condition catalyzes the breakdown of the sugar molecule through the reverse aldol condensation mechanism, to acetaldehyde, glyoxyl, acrylaldehyde (acrolein) and other volatile carbonyl compounds. (Acetaldehyde and glyoxal are commercially highly desirable pyrolysis products.) The products formed through these pathways are further randomized by decarboxylation, decarbonylation and disproportionation reactions which are prevalent under pyrolytic conditions. In the absence of any additives both types of reactions take place. However, the yields and isotopic patterns are closer to those of the acidic than to those of the alkaline condition.

The proposed chemical reactions and mechanisms for different pathways³⁰ provide a foundation for understanding the consecutive and concurrent molecular transformations involved in the pyrolysis and combustion of the cellulosic materials and possible approaches for controlling them. These data indicate that the glycosidic bond of cellulosic materials could be cleaved catalytically under pyrolytic conditions to provide sugar units. Furthermore, it should be possible to catalyze the pyrolysis of the sugar units to promote the formation of char (different types of carbon), furfural, glyoxal, acetaldehyde and other low molecular weight, commercially desirable products. This provides the technical basis for investigations on chemical conversion of cellulosic wastes to these products.

V. RECOVERY AND ANALYSIS OF CELLULOSIC WASTES

Obtaining a relatively uncontaminated fraction of cellulosic waste materials from municipal wastes is a difficult task. Various approaches have been attempted but, seemingly, the more successful methods are air and water classification schemes.

The air classification system injects shredded, dry municipal waste near the top of an air stream flowing upward through a zig-zag column.³⁶ The wastes are separated by the tumbling action of the air currents caused by the zig-zag column and by the velocity of the air flow. With removal of the heavier particles from the bottoms and passage of the successively lighter fractions through several columns in series, as in the schematic diagram of Figure 3, a reasonable degree of separation should be effected. Combining this method with other separation techniques, such as magnetic separation of the ferrous and non-ferrous metals and flotation separation of glass from rubber and wood residues, would make a highly efficient recovery system.

The Black-Clawson Hydropulping facility converts raw garbage into a liquid slurry containing 3 1/2 percent solids.³⁷ The slurry is then separated by a series of screens and centrifugal cleaners into various components as shown in Figure 4. After dewatering, the reclaimed long fibers are sold and the residual paper, plastics and food wastes are mixed with sewage sludge and burned. Ferrous material, glass and aluminum are recovered by other techniques.

To determine the chemical composition and the basic value of the various forms of fibers recovered from municipal wastes several samples were obtained through the courtesy of Mr. Richard Carnes from the Solid

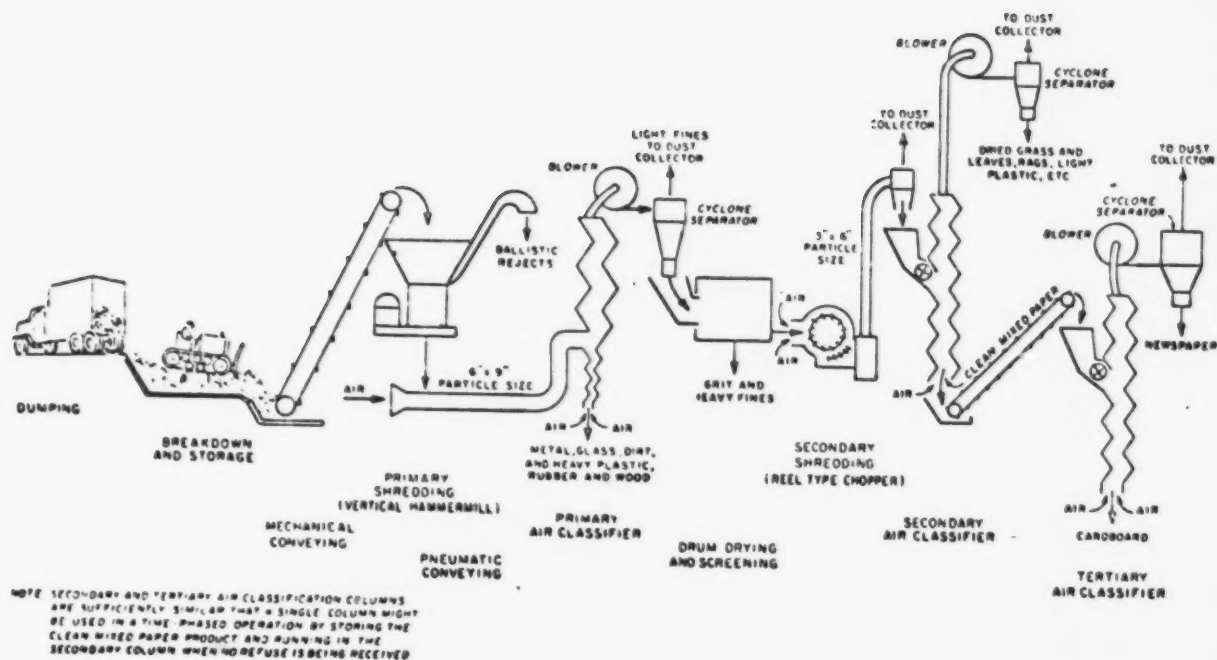


Figure 3. Schematic flow diagram of air-classification process (from reference 36)

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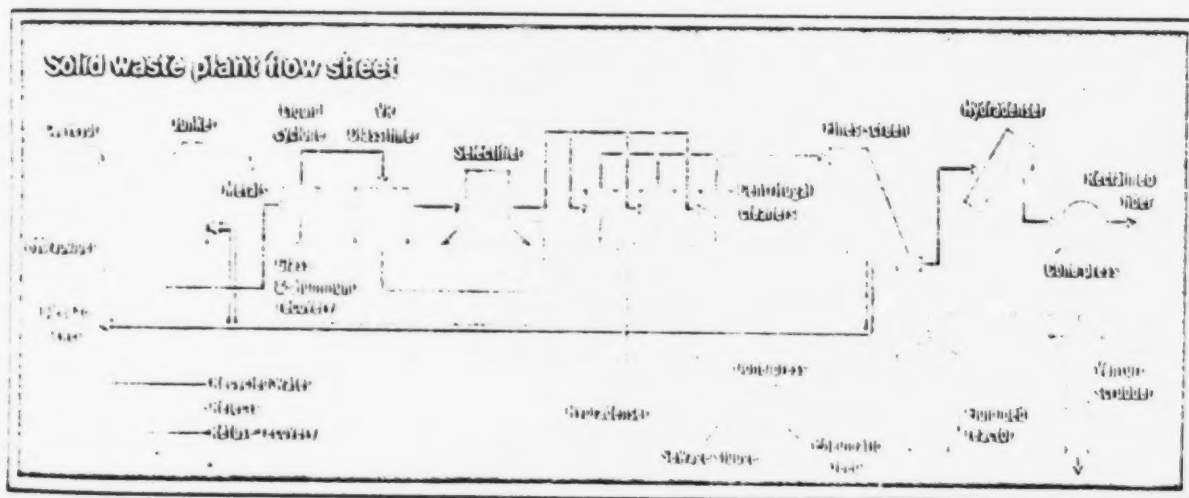


Figure 4. Schematic flow diagram for hydropulper process (from reference 37)

Waste Research Division of the National Environmental Research Center
in Cincinnati, Ohio. These samples consisted of:

- A. Long fibers derived from the Black-Clawson Hydrosieve recovery plant in Franklin, Ohio.
- B. Short fibers produced by the same plant as a mixed by-product which is currently being burned in fluidized bed incinerators.
- C. Short fibers produced by the same plant containing plastic, leather and other hydropulper wastage.
- D. City of Cincinnati garbage, ground and passed through Stanford Research Institute Zig-Zag Air Classifier.

The recovered cellulosic fibers were redried to a constant weight and hydrolyzed to produce the sugar components of the cell wall polysaccharides consisting of cellulose and various forms of hemicelluloses. The resulting sugars were reduced and analyzed as fully acetylated alditols by GLC using established methods (see experimental).

Since the recovered fibers are contaminated with inorganic material which could produce catalytic effects on chemical reaction, it was also important to determine the ash or inorganic content. For these data the dry fibers were combusted in a muffle furnace at 900°C for 6 hours according to ASTM standards and the residual ash was determined gravimetrically.

Further tests were made to determine the amount of extractives, non-hydrolyzable material (Klason lignin) and uronic acids. The results obtained for various forms of recovered fiber are listed in Table 4. experimental data represent the average of three determinations.

Table 4. ANALYSIS OF RECOVERED FIBERS

	-----Sample-----			
	A	B	C	D
Glucose	54.5	32.9	38.4	37.4
Xylose	11.3	4.6	4.7	5.1
Mannose	4.3	3.3	3.5	3.6
Galactose	0.0	0.7	0.5	0.5
Arabinose	0.5	0.4	0.4	0.4
Total Sugar	70.6	41.9	47.5	47.0
Extractives	3.0	20.0	11.7	11.9
Non-hydrolyzable material	6.5	30.7	31.3	35.8
Ash	1.6	23.3	17.4	32.6
Uronic Acids	1.5	---	---	---
Total	83.2	115.9	107.9	127.3

In the above Table, the percentages for samples B, C and D exceed unity because the extractive and non-hydrolyzable material experimental procedures overlap somewhat and certain components of the waste samples will be included in both fractions. Also, soluble salts would appear as part of the extractives as well as ash. Sample A has approximately 17 percent unaccounted for material that is of an organic nature. Analysis of the carbon, hydrogen, and oxygen content of this sample yielded a total of 99.1 percent which is in close agreement with the figure derived from the ash value.

In spite of the overlapping of values in Table 4, valuable information can be obtained. The amount of glucose, which is derived mainly

from cellulose, shows the proportion of this polysaccharide in the fibers. Comparing this figure with the non-hydrolyzable material and ash content serves as a basis to determine the relative worth of these fibers. Thus, Sample A with its low ash and non-hydrolyzable material content would be more adaptable to chemical conversion than the other samples. Also, it is interesting to note that comparing the amounts of cellulose, lignin, and xylose with those of Kraft pulps, which average about 44, 28 and 10 percent,³⁸ respectively, indicates that most of these fibers are derived from products manufactured from this type of low grade pulp.

VI. ACTIVE CARBON

Active carbon is a term applied to an amorphous charcoal that has been selectively eroded to increase both the pore structure and surface area.³⁹⁻⁴¹ The carbonaceous source material is first charred at a low temperature and then "activated" at a higher temperature by the influence of such oxidizing gases as steam, carbon dioxide or air. Alternatively, the char can be activated by heating with a selected catalyst. During the activation process, a series of micro- and macropores is formed throughout the carbon which greatly increases the surface area.⁴² This combination of large surface area and pore structure gives active carbon its adsorptive power.

Adsorption is variously defined,^{40,41,43} but in essence it is the formation of a layer of substrate, from either a vapor or liquid phase, on the surface of a solid. The adsorption of this substrate balances weak forces on the surface of the solid and these weak forces are sufficient to hold the substrate on the surface. The micropores aid in the adsorptive process by "trapping" the substrate molecules. The combination of these

two features allows active carbon to selectively remove various substrates in a stream process.

Commercially, the major market for active carbon is for removing taste and odor-causing materials from drinking water. The market for active carbon for water treatment is expected to double in the five years from 1971 to 1976 to an approximate value of \$10 million per year.⁴⁴ Other large commercial uses are for solvent recovery, cane sugar purification, catalyst carriers, gas purification and air conditioning. All these uses required approximately 160 million pounds of active carbon in 1966.⁴⁵

Several recent developments indicate the diversity of applications of active carbon that could make it a very important material for the improvement of environmental quality. These developments include the almost complete removal of sulfur dioxide from combustion exhaust gases,⁴⁶⁻⁴⁸ removal of ozone from factory air systems,⁴⁹ removal of synthetic detergents during tertiary sewage treatment,^{50,51} and reduction of pollutants from auto exhausts.⁵² These uses clearly indicate the potential importance of active carbon in environmental and industrial applications.

From both technical and economical points of view, conversion of cellulosic waste to active carbon presents an attractive possibility. Technical difficulties in the separation and purification of the products in the volatiles and tar fraction have deterred industrial development. The char, on the other hand, is readily obtainable and by using selected additives, active carbon can be produced fairly easily. It should be noted that production and handling of active carbon do not require extensive facilities and capital outlays. For this reason, such a facility could easily be integrated into a municipal operation which involves collection, separation and disposal of refuse as well as puri-

fication of water and treatment of sewage plant effluents. In such a system, activated carbon is generated from cellulosic wastes and used in the water and sewage treatment plants. Such an integrated method of disposal and purification would benefit the environment and municipality in several ways: a. some of the products recovered by sorting the refuse could be sold; b. transportation costs for shipping active carbon would be eliminated; c. cost of the active carbon would be minimal; d. present disposal techniques would be alleviated; e. better quality water would be available; and f. various expenses added by middlemen would be eliminated.

Initially, experimental plans were to determine the optimum yield and activity of carbon that could be produced by various catalysts. These catalysts were selected for the ability to produce either high yields of char and/or high activity in the char produced from other carbonaceous sources and include zinc chloride, sulfuric acid, phosphoric acid, diammonium sulfate, diammonium phosphate, boric acid, ammonium hydroxide and iron, calcium and sodium salts. Also, these catalysts are readily available and, for the most part, extremely cheap. The activity of the carbon was measured by the standard iodine adsorption test³⁹ and experiments were planned to determine the effects of temperature, time, and weight percent of catalyst. A typical run included mixing the desired proportion of additive with the waste material in an appropriate solvent, drying the mixture, charring the sample at a selected temperature (e.g., 300°) for a selected time, activating the sample at higher temperature (e.g., 800°) for a shorter time, removing the catalyst by washing and then testing for activity.

The use of a catalyst to act as a charring and activating agent obviates the requirement of a second, separate step. However, two other approaches requiring second steps were also tested. In one, a char was produced and then activated by heating to high temperature and admitting an oxidizing gas (superheated steam) into the furnace. In the second process, a char was produced using one catalyst and then activated with another catalyst.

The results of these experiments are shown in Appendix A and can be summarized by noting that some catalysts, notably zinc chloride (AC-6 to AC-11), phosphoric acid (AC-71 to AC-74) and boric acid (AC-93 to AC-96) were quite effective, while others, calcium carbonate (AC-66 to AC-70), calcium hydroxide (AC-85 to AC-88) and copper (II) sulfate (AC-89 to AC-92), produced chars of only moderate activity. Steam activated (AC-1 to AC-5) and doubly-catalyzed (AC-48 to AC-51) samples showed moderate activity. These results indicate that it would be possible to produce various grades of carbon by using different catalysts.

A detailed economic analysis for producing active carbon from wastes on the basis of the above data is beyond the scope of this report, but there are several factors that should be considered; a. the catalyst can be recovered and reused which would be important if zinc chloride were selected since it is a relatively expensive chemical; b. the nature of the activation process requires vessels able to withstand corrosive atmospheres at high temperatures; c. it is possible to recover the waste gases produced from charring and use them as additional fuel for burners; d. the carbon could be used without removal of the cheaper catalysts if a low-grade carbon was desired for use as a pre-treatment for further purification steps.

VII. PRODUCTION OF LEVOGLUCOSAN

In analogy with model compounds, it is expected that heating of cellulose initially results in cleavage of the glycosidic bond by the transglycosylation process. The initial products of this process should be anhydro sugars, which are subsequently dehydrated to give furan compounds, rehydrated to give D-glucose, rearranged internally to the more stable levoglucosan or condensed externally to give polysaccharides.²⁵⁻²⁸ Further heating or presence of some catalysts result in decomposition of the above products which collectively form the tar fraction.

The main component of the tar fraction is levoglucosan or 1,6-anhydro- β -D-glucopyranose. Levoglucosan and its various condensation products in the tar could be readily converted to glucose and, if isolated as pure crystalline material, it could be used as a substitute for sugars or possibly the more costly industrial anhydro sugar derivatives and polyols. Major efforts were directed towards the analysis of the tar fraction and investigation of the basic reactions involved in the conversion of cellulose into these materials, which is being published as a paper on "Pyrolysis of Cellulose" in the Journal of Carbohydrate Research.

This paper, which is attached to this report as Appendix B, shows that pyrolysis of cellulose provides a tar containing various amounts of levoglucosan, chemically known as 1,6-anhydro- β -D-glucopyranose, a related ring isomer called 1,6-anhydro- β -D-glucofuranose, α - and β -D-glucose, 3-deoxyhexulose, other dehydration products of glucose and a variety of poly- and oligosaccharides.

The yield of tar and its content of levoglucosan and other materials that could be readily converted to D-glucose have been determined under several conditions.²⁷

Pyrolysis under vacuum gave nearly 56 percent tar that consisted of 34 percent of levoglucosan containing minor amounts of its ring isomer and 21 percent oligosaccharides and other condensation products that could be readily hydrolyzed or converted to D-glucose (based on the original cellulose).

Pyrolysis at atmospheric pressure substantially reduced the yield of the tarry products because these products could not escape the reaction zone and were further pyrolyzed and decomposed. (The situation may be different in a fluidized bed process, where the products are removed from the reaction zone automatically.) Furthermore, addition of SbCl_3 and a variety of other catalysts lowered the temperature of pyrolysis but lead to extensive dehydration and decomposition.

Composition of the hydrolyzable components of the tar was also investigated. The resulting data are summarized in Reference 27, which showed that these materials are essentially composed of randomly linked oligosaccharides derived from the condensation of levoglucosan.

The above investigation also indicated the basic reactions and mechanism involved in the thermal depolymerization of cellulose and ensuing reactions which reduce the yield of levoglucosan as the major thermal depolymerization product. From this data it is apparent that dehydration and condensation are the two major types of reactions which reduce the yield of levoglucosan.

Contrary to the relatively high yields of levoglucosan obtained with cellulose, only 3.1 percent yields of anhydrosugar were produced under vacuum pyrolysis of waste materials (sample A) and the combined tarry products amounted to only 18.6 percent (Table 5). There could be several reasons for the decreased yields but the most significant factors are probably impurities in the waste altering the course of the pyrolytic reactions and the crystalline nature of the cellulose being altered by processing. These two factors cause variation in the yields of levoglucosan from purer cellulose samples.¹⁶ Since the purity and crystallinity of the cellulosic waste materials is fixed, other means to increase the yield of levoglucosan were sought.

Table 5. PRODUCTION OF LEVOGLUCOSAN FROM CELLULOSE AND WASTE FIBERS

Products	300°, 1.5 mmHg		300°, 8-10 mmHg, steam	
	Whatman CF 11 Cellulose	Sample A	Whatman CF 11 Cellulose	Sample A
Char	15.5%	21.4%	13.0%	19.6%
Tar	52.0	18.6	65.3	34.6
Levoglucosan	29.0	3.1	36.8	2.9
1,6-anhydrogluco- furanose	5.0	0.0	4.1	0.0

A series of experiments were designed to test if a low pressure steam current in the pyrolysis atmosphere was sufficient to counteract the dehydration reactions by which the glucose units decompose. These results (Table 5) show that steam does increase the levoglucosan production for cellulose but not for the waste fibers, even though more tarry material was produced in both cases.

Another series of experiments were conducted using various Lewis acids to test if they could provide more efficient cleavage of the glycosidic bond at lower temperatures. By converting the large molecular weight cellulosic materials to small sugar units, the chemical inertness of cellulose could be reduced. At high temperatures, these same glycosidic bonds are cleaved, but under these conditions, the sugar units which are generated decompose randomly to a variety of secondary pyrolysis products.

Following the initial studies with zinc chloride (ZnCl_2), other catalysts tested were aluminum (III) chloride (AlCl_3), vanadium (III) fluoride (VF_3), iron (III) chloride (FeCl_3), antimony (V) chloride (SbCl_5), antimony (III) chloride, phosphorous (III) chloride and boron (III) fluoride:etherate ($\text{BF}_3 \cdot \text{ET}_2\text{O}$). Unfortunately, none of these treatments were promising and most of them drastically reduced the yield of levoglucosan and enhanced the char formation. The high expense of these catalysts, even though most could be recovered, and the low yields of levoglucosan were deemed sufficient reasons to discourage further research on this approach.

VIII. VOLATILE PRODUCTS

As previously mentioned, the main problem in uncatalyzed pyrolysis of cellulose is the formation of a variety of volatile products, none of which are formed in sufficiently high quantity to make the dry distillation process commercially feasible. Initial experiments with model compounds showed that acidic catalysts increase the formation of furan compounds and alkaline catalysts increase the yield of acetaldehyde and glyoxal. In light of this information, it was decided to investigate alkali catalysis.

In 1829, Gay-Lussac discovered that alkali fusion of carbohydrates yielded considerable amounts of oxalic acid.⁵³ Later, fusion of wood and recovery of oxalic acid from the char by washing became commercially important processes. Now, oxalic acid is produced by more efficient methods. Under fusion conditions, atmospheric oxygen is readily available and is necessary for formation of such secondary oxidation products as oxalic acid. However, the temperature involved is sufficiently high that significant amounts of these volatile products would decompose further if they were not trapped in the char as stable alkali salts. Under pyrolytic conditions, where there is a lack of oxygen, secondary oxidation is not likely to occur but dehydration and rearrangement reactions are expected instead. However, some of the volatile products could remain in the char as various acid, alcohol or enolate salts.

To investigate the possibility of volatile products remaining in the char under alkaline pyrolysis, cellulose was pyrolyzed with varying percentages of sodium hydroxide and the residues dialyzed to recover low-molecular weight compounds. These experiments showed that formation of materials recoverable by evaporation of the dialyzate reached a maximum with addition of 20 percent alkali while formation of total volatile compounds increased with increasing alkali (Figure 5). Since the 20 percent ratio corresponds to a 1:1 molar ratio, the data indicate that further degradation of the more desirable products to small, extremely volatile ones occurs when this ratio is exceeded and that salt formation is most prevalent at this ratio.

Gas chromatographic analysis of the mixture of products recovered by evaporation showed numerous compounds were present. By mass spectroscopy

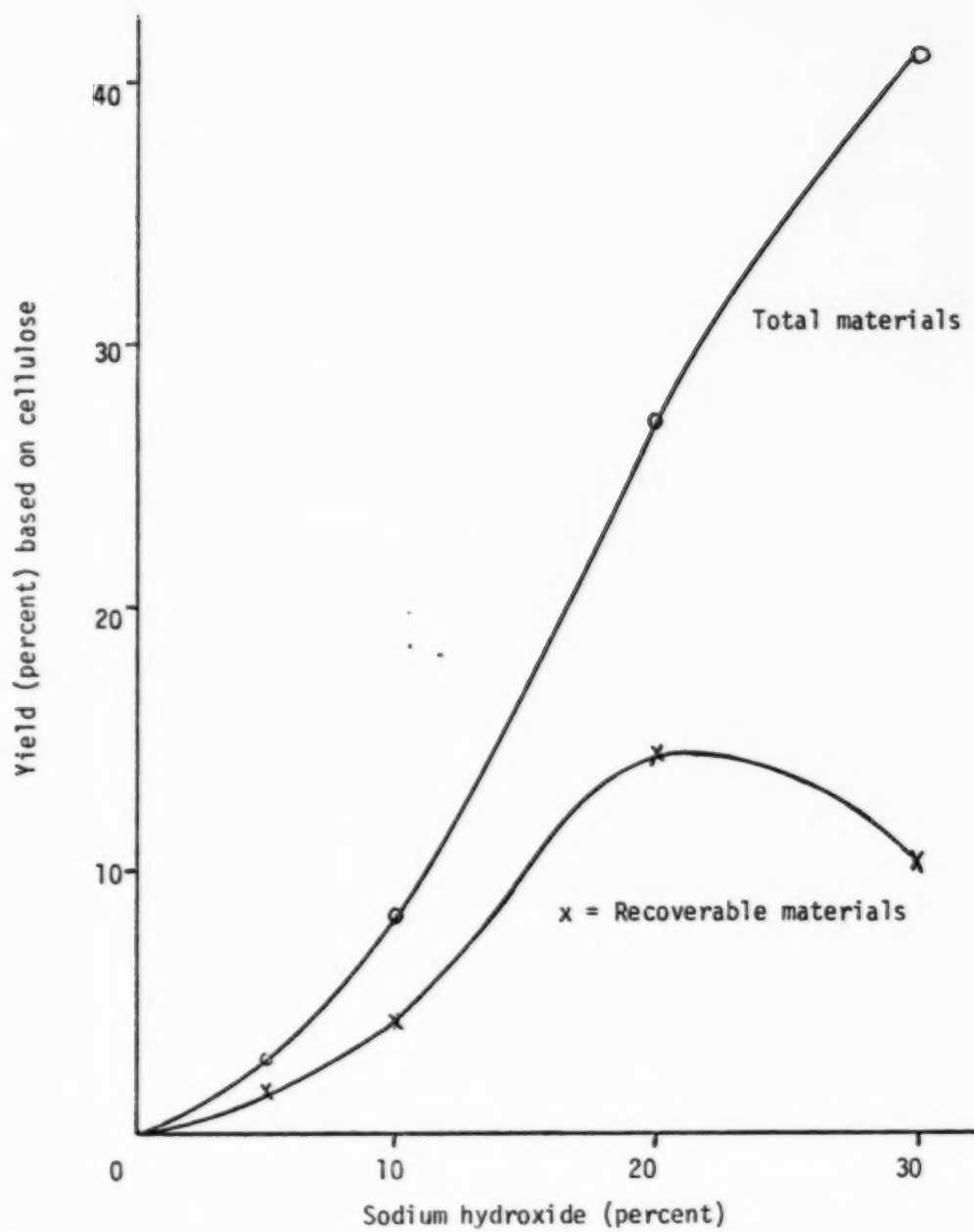


Figure 5. Production of low-molecular weight compounds from alkaline pyrolysis, 300°

and chemical means, 2-furoic acid was positively identified as one component of this mixture and all of the other compounds reacted in a manner characteristic of organic acids. These compounds are probably various keto-acids related to the reductic acids and were not further characterized even though a small amount of one was isolated as a crystalline substance.

This approach was not pursued further since no commercially valuable compounds were detected among the various products in sufficient quantity to make this process feasible. However, the possibility exists that the mixture could be utilized without separation of the components as a substitute for other organic acids.

IX. PRODUCTION OF LEVULINIC ACID

Production of levulinic acid as noted before was added to this project because of the possibility of obtaining relatively high yields of a commercially useful product by rapid processing of cellulosic wastes. This type of rapid processing retains the principal advantage of the pyrolysis approach adapted for this project. Methods of manufacturing levulinic acid from cellulosic wastes and glucose containing carbohydrates in general have been known before and commercial production has been attempted at the pilot plant level without commercial success mainly because of the high cost of the operation.

In such an operation, cellulosic materials are heated with dilute mineral acid to produce levulinic acid and formic acid. The mineral acid is then neutralized and levulinic acid is recovered by solvent extraction and distillation. Principal contributors to the high cost of the operation have been slow and lengthy batch production, requirement of a costly sol-

vent to extract the product, the high cost of sulfuric or hydrochloric acid and ultimately lack of incentive and a large source of waste or cheap raw material. The cost of production, however, may be considerably reduced to improve the chances for commercialized productions in several ways:

A. Recovery of cellulosic materials from municipal refuse provides a large and dependable supply of raw materials, without additional cost of collection and transportation.

B. The price of sulfuric acid is declining due to the new technology to remove sulfur dioxide from the air and convert it to sulfuric acid as a pollution abatement measure.

C. There is a possibility for completing the reactions at high temperature in a few minutes and thus using a continuous process rather than a cumbersome batch operation.

D. Further processing economics may be affected by recycling the acid liquor over fresh supplies of cellulosic materials and avoiding solvent extraction.

E. The possibility of obtaining better yields from waste paper because of lower lignin content as compared to sawdust and waste wood which traditionally have been the cheapest available raw material.

F. The formic acid produced in equimolar amounts with the levulinic acid may be recovered from the volatile hydrolysis products.

Although the relatively high price of levulinic acid currently has precluded large commercial development, the technology had been developed to transform levulinic acid into a variety of chemical intermediates, as shown in Figure 6.⁵⁴ Interesting possibilities include the formation of solvents and polymers of polyvinyl and polyamide types. Also, the sodium salt of levulinic acid has been found to be a very effective anti-freeze.⁵⁵ As a solution, it is less corrosive to engine parts than tap water and the ease of marketing and shipping a solid anti-freeze cannot be overlooked. When available in low cost, levulinic acid could find numerous other applications as a substitute for organic acids and intermediate synthetic compounds.

Production of levulinic acid from cellulosic wastes was investigated first on small scale sealed tube reactions to determine the kinetics of the reactions and the optimum yields from different materials in relation to time, temperature and acid concentration as the principal variables. After reaction and filtration of residual solids, the excess sulfuric acid was precipitated as its barium salt and the yields obtained in these experiments were determined by using a GLC instrument to analyze the concentration of the levulinic acid in the remaining solution. The analytical procedures and standardization methods required for obtaining meaningful and reproducible results for a large number of experiments presented many experimental problems. These problems were eventually solved and the results are given in Table 6.(page 35) The data show that Sample A fibers which contain more cellulose and less inorganics provide a much better yield and maximum yields could be obtained within a total heating time of 25 min. Using 8 percent H_2SO_4 instead of 4 percent provides only a slightly better yield.

Table 7 shows a summary of the maximum experimental yields obtained from different types of recovered fibers, as compared to the theoretical yields based on the total glucose content of the fiber. It should be noted, however, that the experimental yields will be further reduced during the isolation of the levulinic acid. Therefore, several large scale experiments were conducted. Using an autoclave resistant to acids, larger quantities of Sample A were hydrolyzed under conditions similar to those of the small-scale experiments. Here the levulinic acid was isolated by flash distillation of the syrup obtained after the solids were filtered and the excess sulfuric acid precipitated as its calcium salt. Temperature

Table 6 SCREENING EXPERIMENTS ON PRODUCTION OF LEVULINIC ACID AT 200°C

Type of Fiber	H ₂ SO ₄ , %	Time, Min.	Yield, %
Sample A	2	10	<1
"	"	15	<1
"	"	25	5.3
"	"	45	8.6
"	4	15	6.6
"	"	20	13.8
"	"	25	15.5
"	"	30	13.9
"	"	45	10.3
"	8	25	19.9
"	"	30	15.6
"	"	60	12.9
Sample B	4	10	Trace
"	"	20	2.6
"	"	25	5.7
"	"	30	6.0
"	"	45	10.3
"	8	10	Trace
"	"	15	2.6
"	"	20	9.8
"	"	30	13.8
"	"	45	5.4
Sample C	4	10	Trace
"	"	20	2.6
"	"	25	6.1
"	"	30	6.0
"	"	45	10.3
"	8	10	2.8
"	"	20	5.3
"	"	25	5.0
"	"	30	12.1
"	"	45	8.0
Sample D	4	10	Trace
"	"	20	2.1
"	"	25	3.8
"	"	30	9.3
"	"	45	8.5
"	8	10	1.7
"	"	20	7.3
"	"	25	11.8
"	"	30	7.3
"	"	45	8.2

Table 7. COMPARISON OF THE LEVULINIC ACID YIELD
FROM DIFFERENT TYPES OF RECOVERED FIBERS

Type of Fiber	Glucose Content ^a	Theoretical yield of Lev. Acid ^a	Max. Experi- mental yield of Lev. Acid ^a
Sample A	54.5	35.1	19.9
Sample B	32.9	21.2	13.8
Sample C	38.4	24.8	12.1
Sample D	37.4	24.1	11.8

^a Percent of the original fiber

Table 8. LARGE SCALE PRODUCTION OF LEVULINIC ACID AT 200°

Sample A wt., g	H ₂ SO ₄ , %	Volume Acid, ml	Time, min	Yield, %
100	4	600	20	10.1
100	4	600	20	13.0
100	4	1000	20	8.4
50	4	300	25	1.0
50	4	400	25	5.8
50	4	600	25	14.2
50	4	800	25	8.2

control of the autoclave was difficult to maintain and these results vary somewhat due to this problem. Also the ratio of the weight of waste to the volume of acid was varied in the large scale runs because vessel size in the small scale experimental procedure fixed this ratio at 1:6. The results (Table 8) show that approximately 25 percent of the levulinic acid produced is lost in isolation and that more dilute slurries are not necessary.

In addition, one large scale experiment was run after first swelling the waste fibers in anhydrous ammonia. Swelling decreases the hydrogen-bonding of the fiber and increases the "accessibility" of the glycosidic bonds to reagents. In the one experiment, a yield of almost 24 percent by weight levulinic acid was isolated.

These results compare favorably with Chapman's estimate that approximately 9 percent of refuse by weight can be converted to levulinic and formic acid.⁵⁶ Another report shows yields of approximately 17 percent levulinic acid when sawdust was hydrolyzed by the same process.⁵⁷

X. EXPERIMENTAL

Sugar Analysis.-The sugar content of the fibers was determined by acid hydrolysis of the carbohydrate polymers, conversion of the monomers to acetylated alditols and analysis by GLC according to the method of Gunner *et. al.*⁵⁸

Extractives and Non-hydrolyzable Material.-Extractives and non-hydrolyzable material were determined as in the procedure used to analyze for Klason-Lignin in wood.⁵⁹

Ash.-Ash content was determined following the ASTM Standard for paper.⁶⁰

Uronic Acids.-Determination of the uronic acids was done by the Swedish Forest Products Research Laboratory according to techniques developed by Bylund and Donetzhuber.⁶¹

Elemental Analysis.-The percentages of carbon, hydrogen, nitrogen and oxygen determined by Galbraith Laboratories, Inc. were C:44.53, H:6.28, N:0.055, O:48.35.

Active Carbon.-The cellulosic waste (Sample A) received contained over 60 percent water. It was dried to about 5 percent moisture by heating at 105-110° for 4 days and ground in a Wiley Mill (60 mesh screen). The fluffy ground material was thoroughly mixed with a calculated amount of catalyst in an appropriate solvent and dried at 100° which caused charring with some catalysts. Two gram samples of the treated materials were loaded in porcelain boats and pyrolyzed in a tube furnace flushed with nitrogen for various times at different temperatures. The resulting chars were then ground in a mortar, washed to remove the catalyst and dried. After screening to -200 mesh, samples were tested for activity

by the following process which is a modification of Hassler's method³⁹ allowing the investigation of small samples.

A standard iodine solution containing 2.7-2.8 g/l iodine was prepared by dissolving 2.75-2.85 g iodine and 4.1 g potassium iodide in a minimum amount of water and then diluting to 1 l. This solution was kept in dark, stoppered bottles. Sodium thiosulfate solution, 0.1 N was prepared, standardized with iodate and then diluted to 0.01 N. The iodine value of each carbon sample was determined by mixing 0.04 g carbon with 10 ml of the standard iodine solution and 1 ml of 5 percent HCl in a 25 ml flask. After mixing by shaking for 5 min., the samples were filtered through Whatman No.4 paper by gravity. A 5 ml aliquot was then titrated to the starch endpoint using the thiosulfate solution.

Vacuum Pyrolysis.- As described in Reference 27

Steam Pyrolysis.-A tube furnace was equipped with a water container on the inlet and a condenser and two cold traps on the exit. Nitrogen was bubbled through a capillary into the water and the water vapor was preheated before introduction into the furnace. Pyrolysis temperature was 300° and samples were heated 4 hours. The contents of the condenser and traps and the tarry products condensed on the pyrolysis tube were collected, concentrated, and finally dried in a vacuum dessicator. Analysis of levoglucosan content was by GLC of the acetylated derivatives using inositol as an internal standard.

Pyrolysis with Lewis Acids.-Cellulose samples were mixed with calculated amounts of Lewis acids in appropriate solvents to yield 5 percent treatment after freeze-drying. Samples (3 g) were pyrolyzed under nitrogen at 300° for 2.5 hr. Analysis of tar was done as described in Reference 27.

Alkali Pyrolysis.-Samples of cellulose were ground with NaOH under anhydrous conditions (glove bag). Pyrolysis of 1-2 g treated material was at 300° until a constant amount of char was formed. Five percent samples required 4 hours and 30 percent samples less than 5 minutes. The char was ground and dialyzed against 10 x 1 l distilled water over a 5 day period. The combined dialyzate was concentrated to 2 l and after acidification with H₂SO₄, was extracted with ethyl acetate (3 x 500 ml). The extracts were dried with Na₂SO₄ and evaporated. GLC analysis was performed on the methyl derivatives (diazomethane) or the untreated dialyzate using 1/8" x 6' 3 percent OV-17 on Gas Chrom Q, 100-120 mesh columns. Various temperature programming was used.

Levulinic Acid.-Samples (1 g) of ground cellulosic waste material were mixed with 6.0 ml of sulfuric acid solution in a test tube. The test tube was placed in a 1" x 3" stainless steel nipple fitted with caps. One cap was permanently affixed with silver-solder. A rubber stopper was placed on the other end and the cap tightened over it to form a pressure seal. This reaction vessel was then placed in a 200°C. oil bath for the prescribed time. The heat-up time of the reaction vessel was determined to be 4 min. After heating, the vessel was cooled immediately in a cold water bath. The test tube was then removed from the vessel and the sulfuric acid was precipitated and the solution adjusted to pH 2.0-2.2 with saturated barium hydroxide. Then the precipitate and solids were centrifuged out, washed and recentrifuged. (Barium hydroxide is used here to more completely remove the sulfuric acid. Any sulfuric acid remaining in solution could seriously damage the gas chromatograph. Industrially, a cheaper chemical, such as lime (CaO), could be used.)

To the centrifugate and washings was added 1.0 ml of a solution containing 25 g of octanoic acid in 250 ml which served as an internal standard for GLC analysis. The centrifugate was stirred for 30 min. with Dowex 50W-X8 (H⁺ form) to remove excess barium ions and then concentrated on a rotary evaporator with the water bath temperature at less than 60°. The concentrate was then used for GLC analysis. The column was a 1/8" x 10' 10 percent FFAP on 80/100 Gas-Chrom Q. Runs were made isothermally at 225°C.; injection port temperature was 280°C. Integration of peak area was obtained by means of a digital integrator.

The amount of levulinic acid was determined from the responses of the GLC by using the following equation:

$$\text{WT. levulinic acid} = (0.10 \text{ g std})(\text{response constant}) \left(\frac{\text{counts for levulinic acid}}{\text{counts for std}} \right)$$

The response constant was experimently determined.

For the large scale runs, samples were stirred and heated to 200° in a pressurized autoclave. Then, the calculated amount of con. H₂SO₄ was added by blowing sufficient water with nitrogen into a siphon containing the acid so that the siphon emptied into the reaction vessel. This caused a violent, exothermic reaction and it was necessary to bleed off pressure to counter act the reaction and maintain a temperature of 200°±20°. The excessively long heat-up time for the autoclave required that the acid be added this way to prevent reaction during heat-up. Volumes of acid and siphoning water were calculated to yield the desired percentage in the final slurry. After reaction, the residue was filtered, washed with water (4 x 100 ml) and the combined filtrate and washings adjusted to pH 2.1 with Ca(OH)₂. The precipitate of CaSO₄ was removed by centrifugation or filtration, washed with water and the remaining

solution concentrated on a rotary evaporator with bath temperature less than 60° to a thick syrup. The syrup was flash-distilled by suction through a capillary into an evacuated flask maintained at 200° to yield levulinic acid as a pale yellow liquid, that would crystallize upon refrigeration.

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XII. Appendix

Appendix A. ACTIVE CARBONS PRODUCED FROM RECOVERED WASTE CELLULOSE

Sample	Preparation Conditions	% Yield	% I ₂ Removed	<u>g. I₂ removed</u> <u>g. carbon</u>
Darco G-60	Commercial Product		66.6	0.425
AC-1	45 min. at 200°C, 10 min. at 310°, 4 min. steaming at 310°	a	29.0	0.204
AC-2	180 min. at 200°, 60 min. steam- ing at 670-720°	15.4	62.1	0.438
AC-3	270 min. at 200°, 45 min. steaming at 685-700°	14.5	45.7	0.320
AC-4	60 min. at 250°, 30 min. steaming at 700-720°	15.5	62.3	0.438
AC-5	150 min. at 295-305°, 30 min. steaming at 600°	18.0	36.2	0.254
AC-6	90 min. at 600-660°, 100% ZnCl ₂	37.0	97.2	0.678
AC-7	20 min. at 600-610°, 50% ZnCl ₂	31.9	98.5	0.687
AC-8	20 min. at 600-610°, 25% ZnCl ₂	31.9	98.2	0.690
AC-9	20 min. at 600-610°, 10% ZnCl ₂	31.0	88.4	0.624
AC-10	20 min. at 600-610°, 150% ZnCl ₂	40.1	96.9	0.681
AC-11	20 min. at 600-610°, 200% ZnCl ₂	34.8	97.1	0.681
AC-12	20 min. at 600-610°, no catalyst	16.8	32.2	0.225
AC-13	30 min. at 450-500°, 15 min. at 850-900°, 1% H ₂ SO ₄	15.8	46.6	0.323
AC-14	30 min. at 450-500°, 15 min. at 850-900°, 2% H ₂ SO ₄	20.1	36.3	0.252
AC-15	30 min. at 450-500°, 15 min. at 850-900°, 5% H ₂ SO ₄	22.3	51.3	0.358
AC-16	30 min. at 450-500°, 15 min. at 850-900°, 10% H ₂ SO ₄	29.4	31.0	0.215

Appendix A. con't

Sample	Preparation Conditions	% Yield	% I ₂ Removed	$\frac{\text{g. I}_2 \text{ removed}}{\text{g. carbon}}$
AC-17	30 min. at 450-500°, 15 min. at 850-900°, 150% H ₂ SO ₄	23.5	40.2	0.278
AC-18	30 min. at 450-500°, 15 min. at 850-900°, 100% H ₂ SO ₄	b	41.7	0.292
AC-19	30 min. at 450-500°, 15 min. at 850-900°, 1% H ₃ PO ₄	9.4	-	-
AC-20	30 min. at 450-500°, 15 min. at 850-900°, 2% H ₃ PO ₄	12.6	32.4	0.224
AC-21	30 min. at 450-500°, 5 min. at 850-900°, 5% H ₃ PO ₄	15.2	53.1	0.361
AC-22	30 min. at 450-500°, 15 min. at 800-850°, 5% H ₃ PO ₄	17.4	28.3	0.196
AC-23	30 min. at 450-500°, 15 min. at 800-850°, 10% H ₃ PO ₄	20.4	23.1	0.157
AC-24	30 min. at 450-500°, 15 min. at 800-850°, 50% H ₃ PO ₄	b	20.6	0.140
AC-25	30 min. at 450-500°, 15 min. at 800-850°, 100% H ₃ PO ₄	b	39.4	0.271
AC-26	30 min. at 450-500°, 15 min. at 800-850°, 1% (NH ₄) ₂ HPO ₄	13.0	36.3	0.247
AC-27	30 min. at 450-500°, 15 min. at 800-850°, 2% (NH ₄) ₂ HPO ₄	17.4	27.5	0.187
AC-28	30 min. at 450-500°, 15 min. at 800-850°, 5% (NH ₄) ₂ HPO ₄	25.4	22.7	0.154
AC-29	30 min. at 450-500°, 15 min. at 800-850°, 10% (NH ₄) ₂ HPO ₄	27.8	-	-
AC-30	30 min. at 450-500°, 15 min. at 800-850°, 50% (NH ₄) ₂ HPO ₄	44.7	36.6	0.251
AC-31	30 min. at 450-500°, 15 min. at 800-850°, 100% (NH ₄) ₂ HPO ₄	37.0	71.4	0.492

Appendix A. con't

Sample	Preparation Conditions	% Yield	% I_2 Removed	$\frac{g. I_2 \text{ removed}}{g. \text{ carbon}}$
AC-32	30 min. at 450-500°, 15 min. at 800-850°, 2% $(NH_4)_2SO_4$	19.3	23.4	0.162
AC-33	30 min. at 450-500°, 15 min. at 800-850°, 5% $(NH_4)_2SO_4$	25.2	23.8	0.163
AC-34	30 min. at 450-500°, 15 min. at 800-850°, 10% $(NH_4)_2SO_4$	29.1	20.2	0.137
AC-35	30 min. at 450-500°, 15 min. at 800-850°, $(NH_4)_2SO_4$	-	25.7	0.174
AC-36	30 min. at 450-500°, 15 min. at 800-850°, $(NH_4)_2SO_4$	40.6	23.0	0.158
AC-37	30 min. at 450-500°, 15 min. at 800-850°, $(NH_4)_2SO_4$	38.0	26.2	0.178
AC-39	210 min. at 240-250°, 1% $(NH_4)_2HPO_4$	35.4	-	-
AC-40	150 min. at 290-300°, 1% $(NH_4)_2HPO_4$	31.2	-	-
AC-41	180 min. at 290-300°, 2% $(NH_4)_2HPO_4$	29.1	-	-
AC-42	120 min. at 290-300°, 5% $(NH_4)_2HPO_4$	32.3	28.5	0.202
AC-43	120 min. at 290-300°, 10% $(NH_4)_2HPO_4$	36.7	25.2	0.179
AC-44	120 min. at 300-320°, 30 min. at 800-820°, 1% $CaCO_3$	10.1	41.6	0.296
AC-45	120 min. at 300-320°, 30 min. at 800-820°, 5% $CaCO_3$	20.0	32.1	0.229
AC-46	120 min. at 300-320°, 30 min. at 800-820°, 10% $CaCO_3$	25.0	38.8	0.272
AC-47	120 min. at 300-320°, 30 min. at 800-820°, 100% $CaCO_3$	35.7	-	-
AC-48	30 min. at 800-820°, AC-39 with 3 ml H_2O added	47.9	43.9	0.313

Appendix A. con't

Sample	Preparation Conditions	% Yield	% I_2 Removed	$\frac{\text{g. } I_2 \text{ removed}}{\text{g. carbon}}$
AC-49	30 min. at 800-820°, AC-40 with 3 ml 10% H_3PO_4 added	48.1	57.4	0.409
AC-50	30 min. at 800-820°, AC-41 with 3 ml 10% H_3PO_4 added	63.4	47.4	0.335
AC-51	30 min. at 800-820°, AC-41 with 3 ml 10% H_3PO_4 added, dried in oven	90.0	43.4	0.305
AC-52	120 min. at 290-300°, 1% $CaCl_2$	25.3	39.7	0.282
AC-53	120 min. at 290-300°, 5% $CaCl_2$	35.0	42.1	0.299
AC-54	120 min. at 290-300°, 10% $CaCl_2$	b	45.7	0.319
AC-55	120 min. at 290-300°, 100% $CaCl_2$	b	46.7	0.332
AC-56	120 min. at 290-300°, 1% $FeCl_3$	30.3	35.4	0.253
AC-57	120 min. at 290-300°, 5% $FeCl_3$	15.0	40.4	0.288
AC-58	120 min. at 290-300°, 30 min. at 800-820°, 10% $FeCl_3$	37.1	31.6	0.221
AC-59	same as AC-58, 10% $(NH_4)_2Ce(NO_2)_6$	21.2	34.5	0.246
AC-60	30 min. at 800-820°, AC-52	-	54.7	0.390
AC-61	30 min. at 800-820°, AC-53	-	45.7	0.332
AC-62	30 min. at 800-820°, AC-54	-	32.7	0.233
AC-63	30 min. at 800-820°, AC-55	-	32.9	0.230
AC-64	30 min. at 800-820°, AC-56	-	50.4	0.359
AC-65	30 min. at 800-820°, AC-57	-	50.9	0.359

Appendix A. con't

Sample	Preparation Conditions	% Yield	% I ₂ Removed	g. I ₂ removed
				g. carbon
AC-66	30 min. at 800-820°, 1% CaCO ₃	10.0	43.6	0.305
AC-67	30 min. at 800-820°, 5% CaCO ₃	10.5	44.3	0.316
AC-68	30 min. at 800-820°, 10% CaCO ₃	33.3	45.0	0.316
AC-69	30 min. at 800-820°, 100% CaCO ₃	-	-	
AC-70	30 min. at 800-820°, 100% CaCO ₃	-	54.8	0.386
AC-71	120 min. at 290-300°, 90 min. at 800-820°, 100% H ₃ PO ₄	-	93.6	0.664
AC-72	120 min. at 290-300°, 60 min. at 800-820°, 100% H ₃ PO ₄	-	89.3	0.634
AC-73	120 min. at 290-300°, 180 min. at 800-820°, 100% H ₃ PO ₄	-	88.1	0.614
AC-74	120 min. at 290-300°, 180 min. at 600-620°, 100% H ₃ PO ₄	-	82.6	0.580
AC-75	45 min. at 800-820°, 5% NaCO ₃	35.3	26.4	0.183
AC-76	45 min. at 800-820°, 10% NaCO ₃	17.8	26.4	0.184
AC-77	45 min. at 800-820°, 20% NaCO ₃	28.9	32.9	0.233
AC-78	45 min. at 800-820°, 100% NaCO ₃	b	81.9	0.569
AC-79	120 min. at 290-300°, 30 min. at 800-820°, no catalyst	15.9	27.3	0.193
AC-80	30 min. at 800-820°, no catalyst	13.4	24.2	0.171
AC-81	same as AC-79, 5% CaSO ₄	18.2	39.9	0.279
AC-82	same as AC-79, 10% CaSO ₄	18.6	45.7	0.322

Appendix A. con't

Sample	Preparation Conditions	% Yield	% I_2 Removed	$\frac{\text{g. } I_2 \text{ removed}}{\text{g. carbon}}$
AC-83	same as AC-79, 20% CaSO_4	19.0	45.7	0.320
AC-84	same as AC-79, 100% CaSO_4	28.4	50.8	0.353
AC-85	same as AC-79, 5% Ca(OH)_2	17.7	38.9	0.273
AC-86	same as AC-79, 10% Ca(OH)_2	19.8	49.1	0.348
AC-87	same as AC-79, 20% Ca(OH)_2	19.0	65.9	0.462
AC-88	same as AC-79, 100% Ca(OH)_2	13.7	66.4	0.462
AC-89	same as AC-79, 5% CuSO_4	23.4	43.1	0.300
AC-90	same as AC-79, 10% CuSO_4	23.6	35.6	0.253
AC-91	same as AC-79, 20% CuSO_4	27.7	41.8	0.290
AC-92	same as AC-79, 100% CuSO_4	b	76.8	0.533
AC-93	same as AC-79, 5% H_3BO_3	23.5	55.3	0.392
AC-94	same as AC-79, 10% H_3BO_3	29.7	66.4	0.450
AC-95	same as AC-79, 20% H_3BO_3	32.2	63.5	0.446
AC-96	same as AC-79, 100% H_3BO_3	b	82.9	0.578
AC-97	same as AC-79, sample immersed in con. NH_4OH for 3 months	-	31.9	0.223

^a Sample not completely charred.

^b Sample severely charred by catalyst during drying.